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Deposition of LDH on plasma treated polylactic acid to reduce water permeability

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ABSTRACT

A simple and scalable deposition process was developed to prepare polylactic acid (PLA) coatings with enhanced water barrier properties for food packaging applications. This method based on electrostatic interactions between the positively charged layers of layered double hydroxides (LDHs) modified with ionic liquids (ILs) and the negatively charged plasma treated polylactic acid leads to homogeneous, stable, and highly durable coatings. Deposition of the LDH coatings increases the surface hydrophobicity of the neat PLA, which results to a decrease in water permeability by about 35%.

1. Introduction

In order to improve functionality and performance, several technologies have been developed over the years including incorporation of a number of active substances into packaging materials. Such active packaging technologies are designed to extend the shelf life of food while maintaining their nutritional quality and safety. Active packaging technologies typically involve some interactions between the food, packaging material, and the internal gaseous atmosphere. Oxygen and moisture scavenging and antimicrobial activity are some of the functions that have been incorporated into active packaging [1–3]. Another technology is based on nanocomposites wherein inorganic nanoparticles of different chemistry or morphology have been incorporated into the polymer matrix. For example, addition of 5 wt.% nanoclay to PET leads to a modest decrease in water vapor transmission of about 15–20% [4,5]. Improvements of water permeability in nylon, a polymer commonly used in packaging applications, have proved to be more difficult [6,7]. Same challenges have been encountered for polycaprolactone (PCL) [8,4].

Besides food packaging, polymer nanocomposites especially clay nanocomposites have attracted widespread interest in recent years. This interest has been fueled by the promise of improved performance and design flexibility and lower cost. Despite this promise, and the consistent efforts by research groups worldwide, persistent challenges with poor miscibility, dispersion, and interfacial control have prevented nanocomposites from realizing their full potential.

Recently, bio-based packaging materials such as poly(butylene succinate) (PBS) or poly(lactid acid) (PLA) have attracted much R&D attention due to their biodegradability [9]. However, these biodegradable polymers suffer from high water vapor permeability, which limits their practical use as food packaging materials [10].

Various coating technologies such as physical vapor deposition, deposition of polymer films from solution (dip-, roll-, spin-coatings), or plasma treatment have been already developed to meet specific needs including improvement of barrier performance [11–13]. Others have used coextrusion to produce coated polymers [14]. However, there are some disadvantages such as degradation of mechanical properties (strain at break) or adhesion failure. More recently, Hirvikorpi et al. have studied Al_2O_3 coatings by atomic layer deposition as well as the use of a non-toxic polyelectrolyte multilayer (PEM) film deposited layer-by-layer on a PLA substrate. A double coating of PEM + Al_2O_3 was necessary to improve the water vapor barrier properties [15]. Plasma treatment has also been used to improve gas and water barrier properties as well as to promote adhesion or the compatibility between the coating and the substrate [16–18]. Recently, our group demonstrated a simple process of depositing functionalized silica nanoparticles

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on plasma treated polymers. [19–21]. Due to the electrostatic interactions between the charged nanoparticles and the plastic substrate, stable and durable coatings have been obtained. More importantly, the silica coatings endow the substrate with superhydrophilic properties [22,23].

Here, we present a simple and scalable approach to modify the surface properties of PLA. Stable and durable coatings based on layered double hydroxides (LDHs) surface modified with ionic liquids can be deposited in one step, increasing the hydrophobicity of the PLA surface and decreasing water permeability by 35%. The process is based on plasma treatment to create negatively charged groups on the surface of the PLA and relies on the electrostatic interactions between the positively charged LDH layers and the negatively charged polymer.

Layered double hydroxides (LDHs), represented by the chemical formula $[M^{II}_{1-x}M^{III}_{x}(OH)_2]A^-$, where M^{II} and M^{III} are di- and tri-valent metal ions, and A^- the interlayer anion balancing the positively charged layers [24,25]. They have received considerable attention in several fields including catalysis, medicine, and as sorbents due to their capacity to adsorb inorganic and organic anions or to release active molecules such as antimicrobials, antioxidants, and oxygen scavengers [26,27]. Our group has focused recently on LDHs modified with ionic liquids (ILs). ILs are organic salts with typical melting temperature below 100 °C. Their excellent thermal stability and low vapor pressure have made them good candidates as "green" solvents for many industrial applications [28]. In addition, they can be used as surfactants, plasticizers, or building blocks for many polymers leading to materials with enhanced properties [29–32].

2. Experimental section

2.1. Materials

$Al(NO_3)_3{\cdot}9H_2O$, $Mg(NO_3)_2{\cdot}6H_2O$ (analytical pure) and NaOH were supplied from Sigma Aldrich and were used as received. Trihexyltetradecylphosphonium decanoate and trihexyltetradecylphosphonium dodecylsulfonate abbreviated as P1 and P2, respectively, were provided by Cytec Industries Inc. Polylactic acid with a melt flow index of 10–25 g/10 min and 9% crystallinity (7032D) was obtained from NatureWorks. Modified Mg–Al LDH with two phosphonium ionic liquids was synthesized by coprecipitation as described previously [33]. In brief, Mg–Al–NO_3 was dispersed in 200 mL of THF. The amount of phosphonium ionic liquid added was about 2 AEC [33]. The suspension was mixed and stirred at 60 °C for 24 h. After filtration, washing and evaporation of the solvent, the treated-LDH was dried at 80 °C for 12 h. Details of the different samples are summarized in Table 1.

PLA films with a thickness of 600 μm were molded in a Carver laboratory press between two Teflon sheets, at 200 °C. Using contact angle measurements, the optimum conditions for plasma treatment were established at 100 W for 30 s. The contact angle decreases from 71° for pristine PLA to 57° for the treated sample. [34].

LDH coatings on PLA were synthesized by first dispersing 500 mg of LDH-P1 or LDH-P2 by ultrasonification (2 min for two times) in 50 ml of water. Then, the plasma treated PLA films were immersed in the LDH suspension in water for 15 min. The films were washed with water and dried at 30 °C.

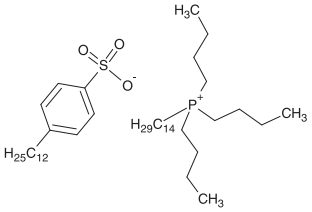
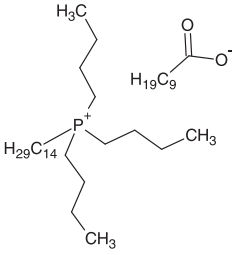
2.2. Methods

Wide-angle X-ray diffraction spectra (WAXD) were collected on a Bruker D8 Advance X-ray diffractometer operating at 45 mA and 33 kV. A bent quartz monochromator was used to select the Cu $K\alpha_1$ radiation (k = 0.15406 nm).

Surface energy of modified LDHs and PLA coatings was determined with the sessile drop method using a GBX goniometer. From contact angle measurements performed with water and diiodomethane as probe liquids on disks obtained from powders by pressing, polar and dispersive components of surface energy were determined using the Owens–Wendt theory [35]. The water droplets (deionized water from Millipore purification system) were monitored by a CCD camera and analyzed by standard drop-shape analysis methods.

Plasma treatments were carried out using a Glen 1000 Resist Strip system with an oxygen plasma source. The tool can be set up to give direct ion bombardment or in a downstream ion mode for lower surface damage. Substrates were treated with an Ar–O_2 (50:50) mixed-gas plasma using a power of 100 W for 30 s.

Table 1
Summary of pristine LDH and phosphonium ionic liquid-modified layered double hydroxides.

Trade name	Intercalant	Designation
	NO_3	LDH-NO_3
IL201		LDH-P1
IL103		LDH-P2

2.3. X-ray photoelectron spectroscopy (XPS) measurements were carried out in an Xps surface instrument SSX-100 UHV

SEM measurements were performed on a Keck Field Emission Scanning Electron Microscope (FE-SEM), LEO 1550 model. High-resolution images (1 nm at 20 keV and 2.5 nm at 5 keV) were obtained.

Transmission electron microscopy (TEM) images were obtained on an FEI Tecnai T12 field-emission electron microscope with an accelerating voltage of 80 kV, using microtomed epoxy-embedded ultrathin samples. The samples were cut using an ultramicrotome equipped with a diamond knife to obtain 60 nm thick ultrathin sections and placed on copper grids.

Water vapor permeability (WVP) tests were performed on uniform films (approximately 130 μm thickness) sealed on the top of plastic cups containing distilled water. Cups were left to equilibrate in desiccators partially filled with saturated water solution of $Mg(NO_3)_2$ to maintain a humidity of 53%. The test temperature was 25 ± 2 °C. The weight of the cups was recorded regularly. The water vapor transmission rate was normalized with respect to the film thickness. The WVP was calculated using the equation WVP = (weight loss x film thickness)/(time × film area × vapor pressure). For each material, three samples were tested with good reproducibility and the data reported hereafter are the average values.

3. Results and discussion

Layered double hydroxides belong to the general family of layered compounds with positively charged lamellae ($[M^{II}_{1-x}M^{III}_{x}(OH)_2]^{x+}$), where M^{II} and M^{III} represent divalent and trivalent ions, respectively,

and A^{x-} anions that balance the charge between the layers. They typically remain well-dispersed in water without any tendency for agglomeration [36].

Before treatment with the IL, the basal spacing of the pristine LDH (LDH-NO_3) is $2\theta = 10.3°$ corresponding to a basal spacing of 0.76 nm spacing of 0.77 nm [37,38,33]. After treatment with the phosphonium salts, the basal spacing shifts to a lower angle. LDH-P1 displays a diffraction peak at $2\theta = 3.2°$, which corresponds to a basal spacing of 2.7 nm (Fig. 1). The corresponding values for LDH-P2 are 2.6° and 3.4 nm. These values are consistent with layered silicates modified with ionic liquids [37,39].

The contact angle and surface energies of the IL treated LDHs were determined by the sessile drop method on pressed powder samples and are summarized in Table 2.

In both case, phosphonium based ILs lead to more hydrophobic LDHs consistent with our earlier work [33]. We hypothesize that the steric hindrance of phosphonium salts (arising from both the cation and anion) due to the presence of long alkyl chains causes a significant decrease in the surface energy of LDH. The IL with the dodecylsulfonate anion leads to the most hydrophobic surface.

It is well-known that the surface of PLA becomes negatively charged after plasma treatment as various reactive species including radicals and ions generate oxygen containing groups on the surface [40,23]. The plasma treatment leads conveniently to the formation of various surface groups on the polymer without sacrificing any of its bulk properties. [41].

PLA can be easily coated with LDH by immersing a freshly prepared plasma treated sample into a suspension of LDH in water (Fig. 2). The positively charged layers of LDH interact with the negatively charged polymer surface to produce a multilayer of positively charged layers separated by anions in the interlayer.

X-ray photoelectron spectroscopy was used for chemical characterization of the pristine, plasma treated, and LDH coated PLA. The results are summarized in Table 3.

As expected, an increase in the oxygen content and the O/C ratio is observed after plasma treatment of the PLA. The O/C ratio increases from 0.39 to 0.57 after plasma treatment. After deposition of LDH-P1 and LDH-P2 (AC) on plasma treated PLA, other elements consistent with the chemical formula of LDH are present. In fact, the Mg/Al molar ratio of 2 seen be XPS is consistent with the stoichiometry of the LDH used and confirming that LDH has been deposited on the PLA surface [42]. The presence of P and S (for one of the samples) further confirms that the IL modified form of LDH is present.

The effective thickness and homogeneity of the LDH coatings were analyzed by transmission electron microscopy. TEM micrographs of PLA film coated with LDH-P1 and LDH-P2 are shown in Fig. 3.

The deposition of LDH-P1 on the PLA surface (Fig. 3a) results in a multilayer coating with a homogeneous coverage of about 20 nm of thickness. A thicker coating of about 80 nm is obtained when LDH-P2 is used (Fig. 3b). All images confirm that a complete and uniform coverage of the polymer surface is obtained in a single coating cycle (i.e., after immersion to the aqueous suspension of nanoparticles and solvent evaporation followed by repeated washings in water).

As a complement to the TEM, scanning electron microscopy images were obtained. The LDH coated samples can be easily dis-

Table 2
Polar and dispersive components of the surface energy of pristine and IL modified LDHs.

Layered Double Hydroxide (LDH)	Θ_{water} (°)	Θ_{CH2I2} (°)	γ polar (mN m^{-1})	γ dispersive (mN m^{-1})	γ total (mN m^{-1})
LDH-NO_3	59.4 ± 0.5	40.3 ± 0.8	13	40	53
LDH-P1	79.1 ± 0.2	59.6 ± 0.5	7	29	36
LDH-P2	86.4 ± 0.1	52.1 ± 0.6	3	32	35

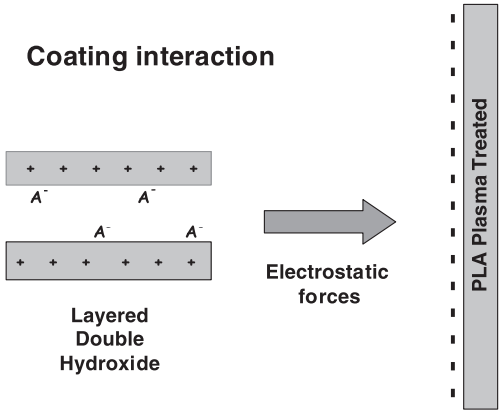


Fig. 2. Schematic of LDH deposition on plasma treated PLA.

Table 3
Elemental analysis from XPS spectra.

Samples	Element	O (1s)	C (1s)	Mg (2s)	Al (2p)	P (2p)	S (2p)
	Binding Energy Position (eV)	529	280	83	69	137	163
PLA UT		27%	69%				
PLA AP		35%	61%				
PLA/AP/AC/LDH-P1		33%	42%	8%	4%	0.4%	
PLA/AP/AC/LDH-P2		34%	49%	8%	4%	0.4%	1%

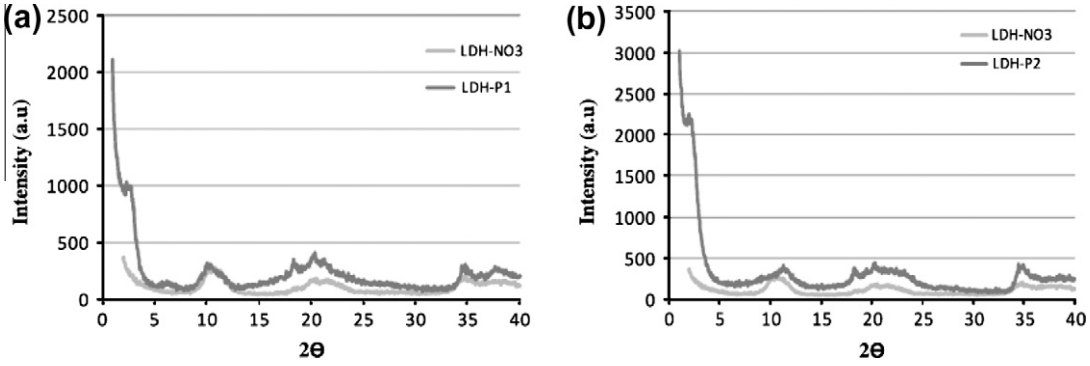


Fig. 1. X-ray diffraction patterns of pristine and IL treated LDHs: (a) LDH-NO_3/LDH-P1 and (b) LDH-NO_3/LDH-P2.

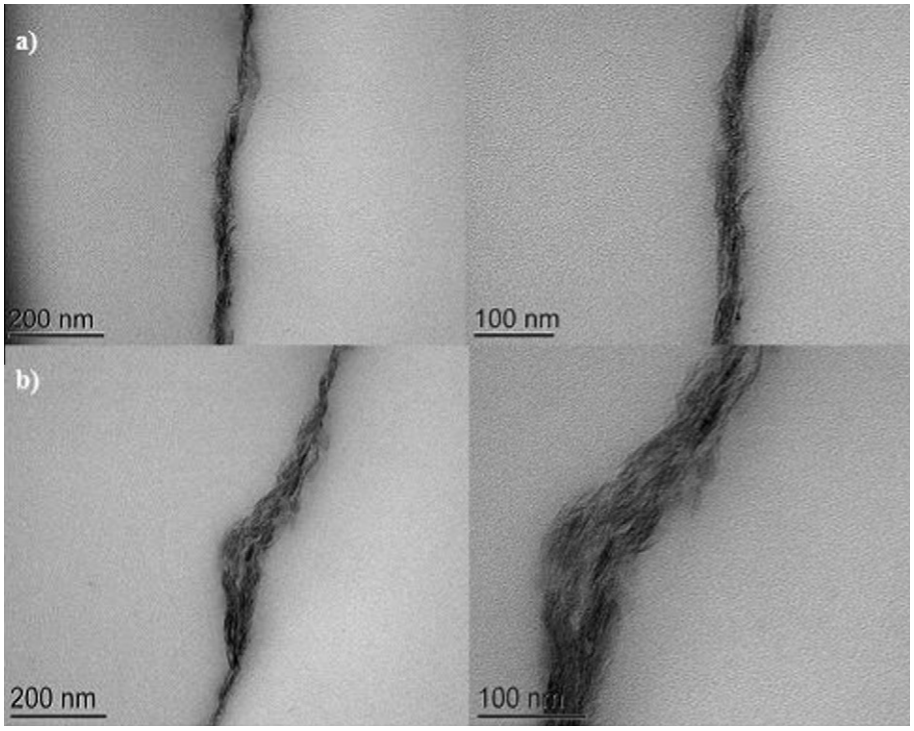


Fig. 3. TEM images of the plasma treated PLA surfaces coated with IL modified LDH nanoparticles: (a) LDH-P1 and (b) LDH-P2.

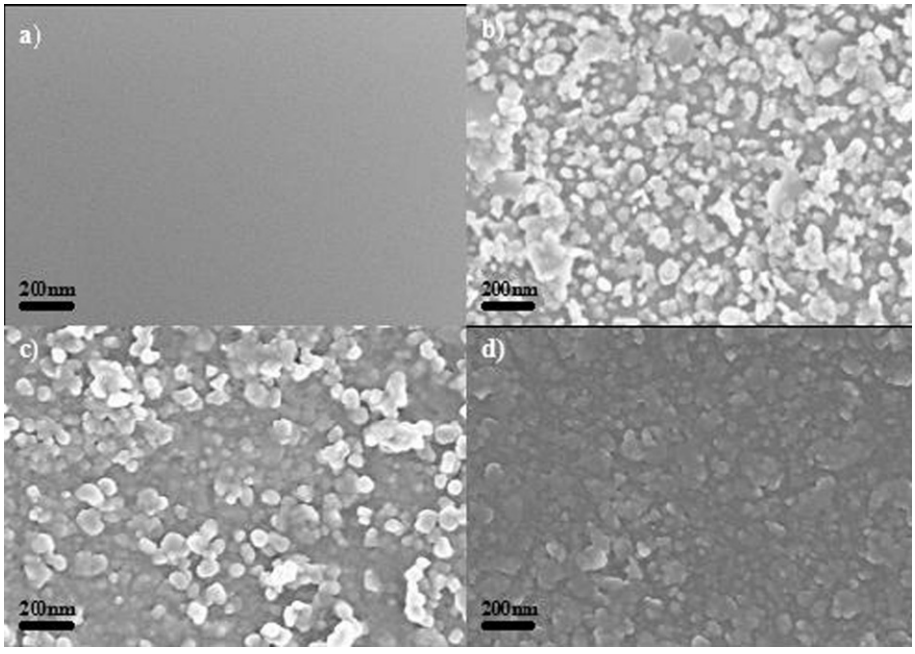


Fig. 4. SEM images for: (a) PLA after Plasma (AP), (b) PLA/AP/AC/LDH-P1, (c) PLA/AP/AC/LDH-P2, and (d) PLA AP/AC/LDH-P2 after 1 h in water.

tinguished from that of PLA, which appears very smooth. The polymer is coated with 60–80 nm LDH nanoparticles.

To evaluate their stability and durability, the LDH coated PLA sample was subjected to ultrasound for 1 h while being suspended in different solvents (water, ethanol). The samples were then imaged by SEM. Even after 1 h of sonication, a homogeneous coating can be seen. As shown in Fig. 4d, the coatings resist detachment and are virtually unchanged, confirming that the electrostatic interactions between the LDH nanoparticles and the charged polymer impart stability and durability to the coatings.

The surface properties of the coatings were evaluated by contact angle measurements (Fig. 5). As expected, the increase in oxygen content on the PLA surface after plasma treatment is accompanied by a decrease in the contact angle (from 71° to 60°) consistent with a more hydrophilic surface.

After deposition of the LDH nanoparticles, the water advancing contact angle increases to 95° and 100° for LDHP1 and LDHP2, respectively. Wetting of a textured surface from a given solvent critically depends upon the surface–solvent chemical affinity as well as certain topological characteristics of the surface such as

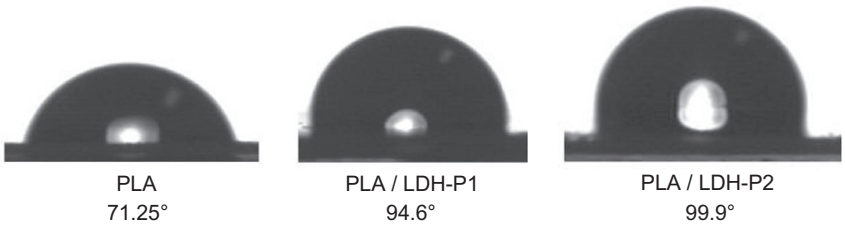


Fig. 5. Advancing water contact angle (°) values of pristine and plasma treated PLA samples: PLA, PLA after plasma (AP) and after coating (AC) with different LDHs, that is, PLA/LDH-P1 and PLA/LDH-P2, respectively.

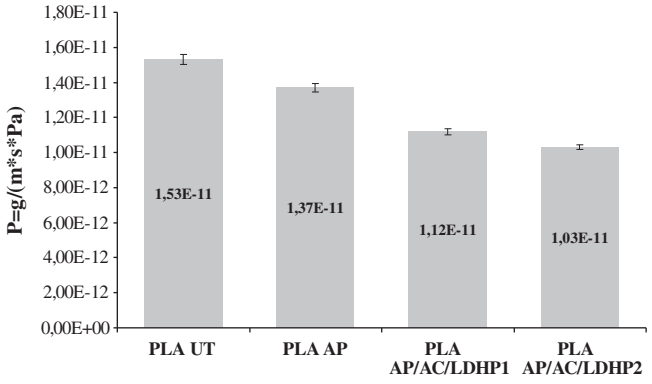


Fig. 6. Water permeability for PLA UT, PLA AP, and PLA AC with different LDH.

roughness and porosity [43,44]. The measurements suggest a change in the wetting characteristics and a more hydrophobic surface after the LDH coating. However, whether this is because of the chemical nature, the induced surface topography or a combination of the two is not presently clear. There already exists extensive literature on altering the wetting characteristics of planar substrates. Various approaches include deposition of thin films of titania [45], hollow silica spheres [46], silica nanoparticles [47,48], or titania–silica alternating multilayers [49] based on layer-by-layer assembly.

This increase in the hydrophobicity of the PLA is similar to that observed by fluorination of the polymer surface through fluorine radicals generated in a fluorine containing plasma [50–52]. However, despite the increase in hydrophobicity of PLA after the surface treatment with the SF_6 plasma, no improvement in water barrier properties was observed [52].

Water permeability of the samples was evaluated by monitoring the weight of containers covered with a PLA film and exposed to a 53% relative humidity chamber. The permeability was calculated from the slope of the weight loss over time dependence according to the equation

$$\mathrm{WVP} = \mathrm{md}/(\mathrm{tAP}) \quad (1)$$

where m is the weight loss, d and A the thickness and area of the film, t is the elapsed time, and P the water partial pressure. The results for neat and LDH modified PLA are presented in Fig. 6.

The water permeability decreases somewhat after plasma treatment but more significantly (35%) after deposition of LDH. For many years, several groups including ours have focused on developing polymer nanocomposites with improved barrier properties. All these efforts have centered on incorporating different types of nanoparticles including clay and LDH because of their platy nature into the polymer matrix with mixed results. A major challenge in these systems is nanoparticle dispersion which has prevented nanocomposites from reaching their full potential. The present work shows that for some properties including barrier, a surface coating can function as if not more effectively. We note that such an approach avoids the challenges of incorporating the nanoparticles into the polymer matrix and the associated processing issues including dispersion and deterioration of mechanical properties (e.g., toughness). Compared to other methods, our approach is simple and effective in enhancing the water barrier properties of PLA, which might pave the way for its use as biodegradable packaging material.

4. Conclusions

In this paper, we present a new, simple, and scalable approach to modify the properties of PLA by depositing an LDH coating on plasma treated polymer. The presence of electrostatic interactions between the positively charged layers of the LDH and the negative charges created on the surface of the PLA treated with plasma produces multilayer coatings in one deposition step that are quite stable and durable. Plasma treatment increases the hydrophilicity of the PLA surface, but deposition of the LDH coatings increases hydrophobicity to values even higher than PLA. The effect might be a combination of the hydrophobic IL modified LDHs or the increased roughness associated with the LDH coatings. More importantly, the LDH coated PLA shows a decrease in water permeability by about 35%. These coatings might be useful in future food packaging applications.

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